85M1022006D

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
MAY 2011		**00-00-2011 to 00-00-2011**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Field-Scale Treatability Study for Enhanced In Situ Bioremediation of Explosives in Groundwater: BioBarrier Installation and Hot Spot Treatment Using DPT Injection	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **The Shaw Group Inc,4171 Essen Lane,Baton Rouge,LA,70809**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
Presented at the NDIA Environment, Energy Security & Sustainability (E2S2) Symposium & Exhibition held 9-12 May 2011 in New Orleans, LA.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**47**	

Field-Scale Treatability Study for Enhanced In Situ Bioremediation of Explosives in Groundwater: BioBarrier Installation and Hot Spot Treatment Using DPT Injection

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The Shaw Group

Richard Meadows, USACE, Huntington, WV

Agenda

- Introduction
- Technology Description
- Carbon Source Comparison
- BioBarrier
- SE Hot Spot 1
- SE Hot Spot 2
- SE Hot Spot 3
- Conclusions

Introduction

- West Virginia Ordnance Works (WVOW) was a TNT manufacturing facility from 1942-1945
- The WVOW site is located on the east bank of the Ohio River, six miles north of Point Pleasant, WV
- WVOW included 12 TNT production lines
- TNT production resulted in soil and groundwater contamination
- Complete decontamination was not achieved, so portions were transferred to the state of West Virginia for use as a wildlife management reserve
- The site is now the McClintic Wildlife Management Area

WVOW TNT Manufacturing Area

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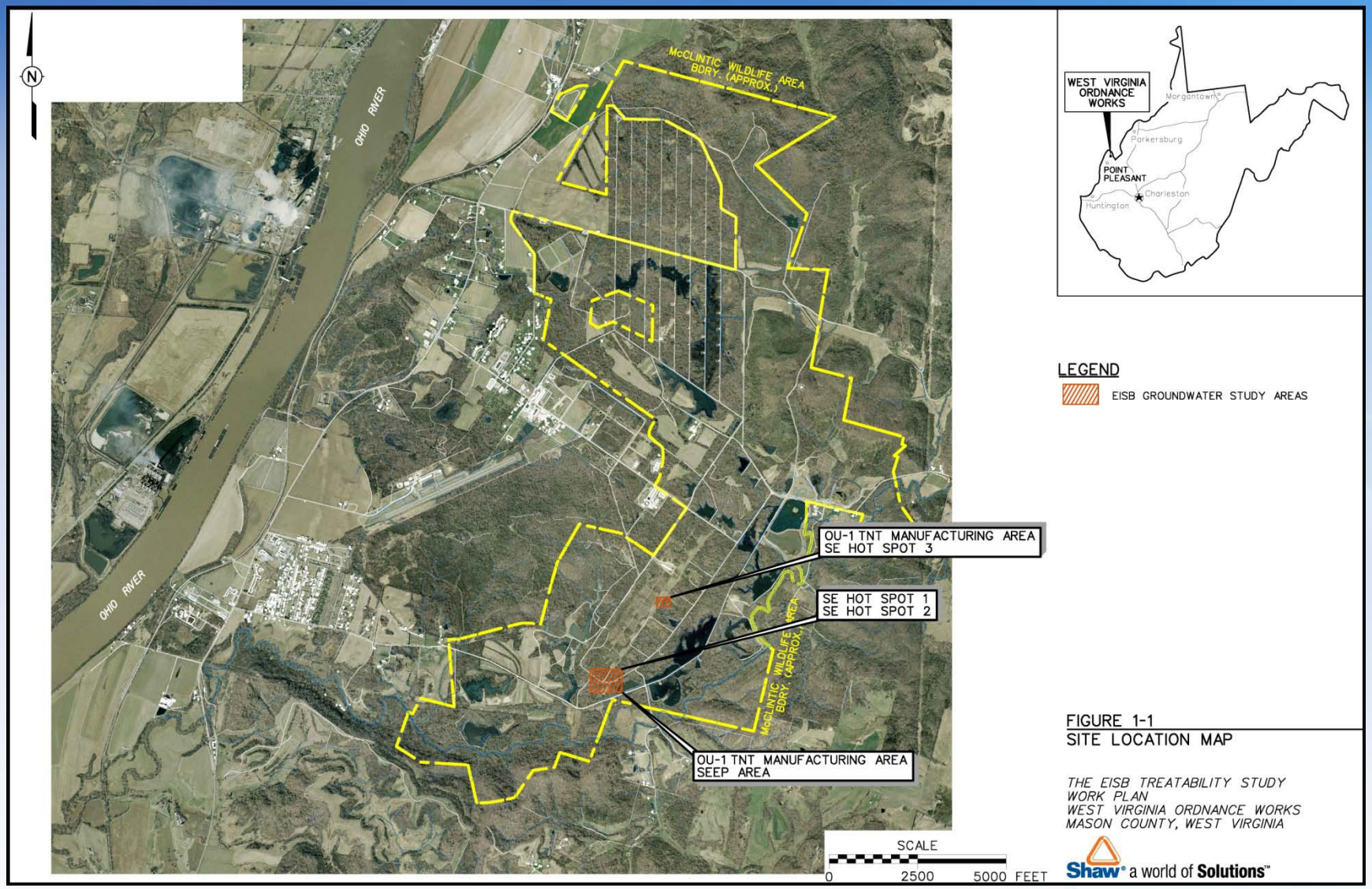
EISB Study Area



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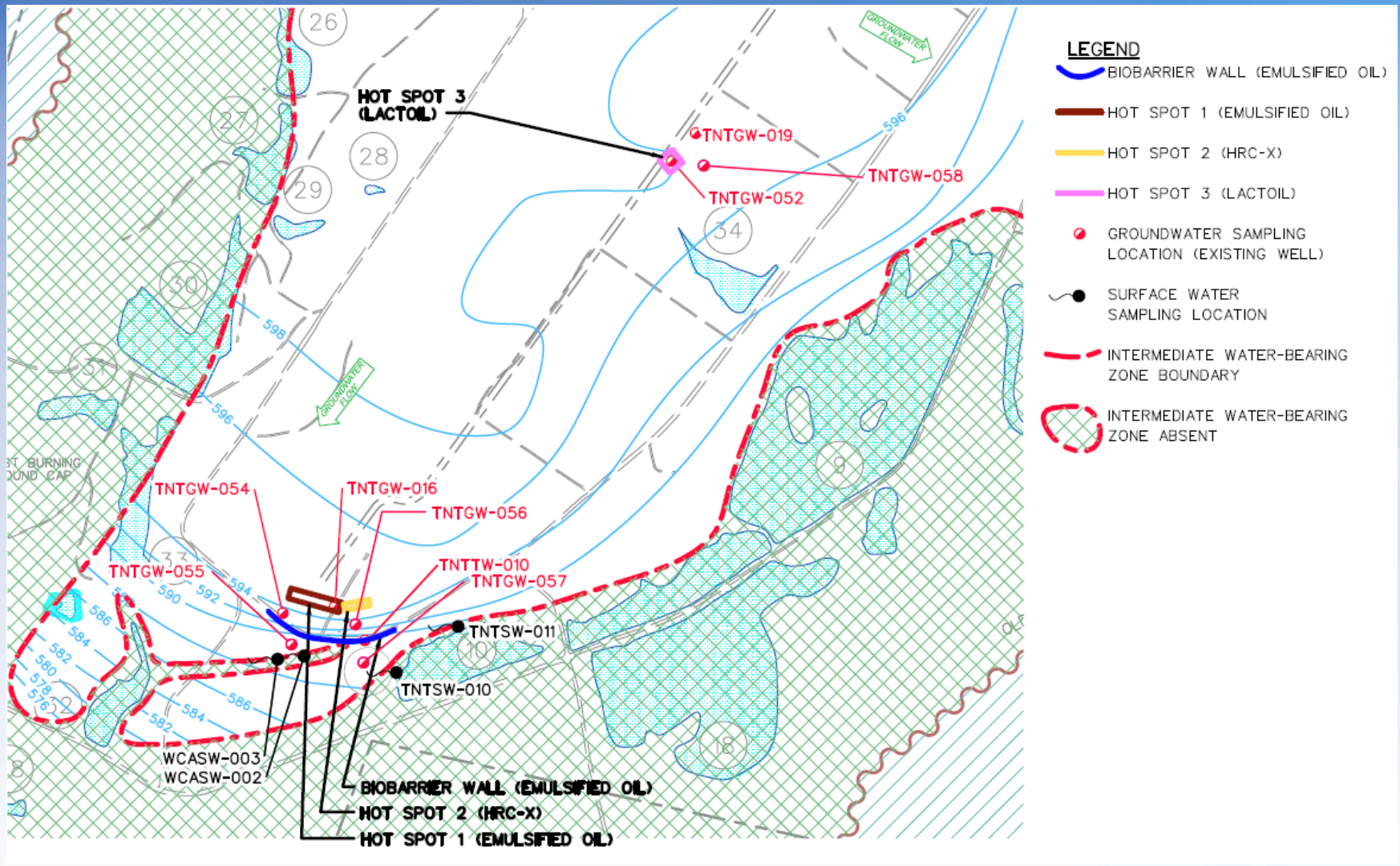
Introduction (continued)

- Four study areas; Seep Area, SE Hot Spot 1, SE Hot Spot 2, and SE Hot Spot 3
- Primary chemicals of concern (COCs) include: 2,4,6-Trinitrotoluene (TNT), 2,4-Dinitrotoluene (2,4-DNT), 2,6-DNT, 2-Amino-4,6-DNT (2ADNT), and 4-Amino-2,6-DNT (4ADNT)
- Enhanced in situ bioremediation (EISB) was selected for field-scale evaluation
- Three different carbon sources are being compared for their effectiveness: SRS™ -Emulsified Vegetable Oil (Terra Systems, Inc.), HRC-X™ (Regenesis), and LactOil™ (JRW)
- The study is focused only on groundwater treatment

Introduction (continued)

- Soil Retention Tests were performed to confirm adequate injection solution concentration
- Slug tests were performed to determine hydraulic conductivity and groundwater flow rate
- Baseline sampling was performed prior to injection of the carbon source in the study areas
- Nine wells and four seep locations were sampled
- Performance sampling was conducted quarterly after injection
- Sampling will continue on a quarterly basis for the first year followed by semi-annual sampling for a second year
- A comprehensive evaluation report will be prepared at the conclusion of the study

EISB Study Area



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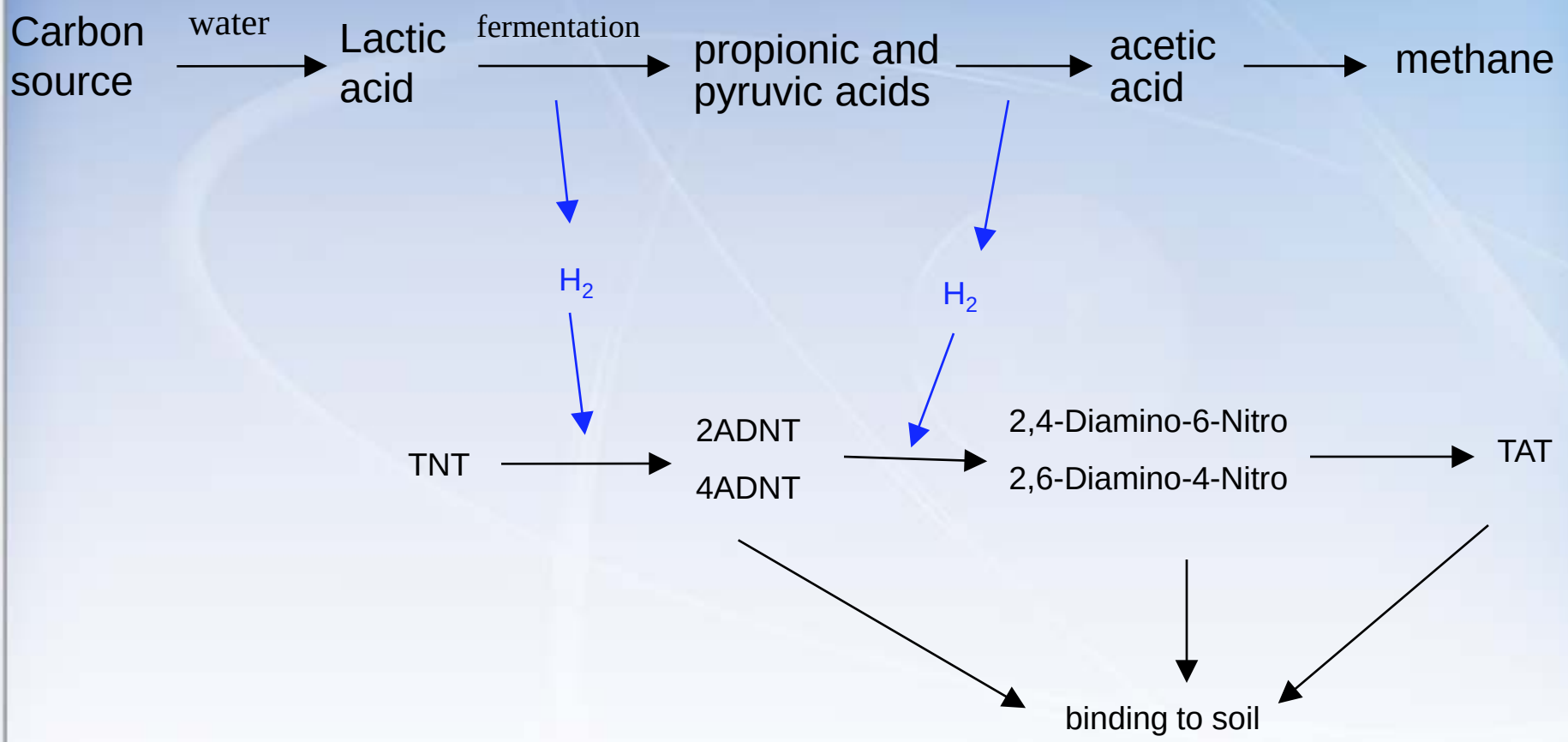
Technology Description

- EISB is a process where a reducing environment is created for indigenous microorganisms
- A carbon source is injected into the aquifer, which provides an energy source for indigenous microorganisms
- As carbon is consumed, O_2 is depleted until the system becomes anaerobic
- After O_2 is consumed, anaerobic fermentation begins and H_2 is released into the system
- H_2 is consumed in competing reactions – reduction of electron acceptors and reduction of nitroaromatics

Carbon Source Degradation and TNT Biodegradation Pathway



Carbon Sources Used

- SRS™, Emulsified Vegetable Oil was used for the Seep Area (BioBarrier) and SE Hot Spot 1
- HRC-X™ was used for SE Hot Spot 2
- LactOil™ was used for SE Hot Spot 3

Carbon Source – SRS

- SRS™, Emulsified Vegetable Oil
  - SRS is a slow release substrate comprised of a mixture of emulsified oil (50-70%) and sodium lactate (< 5%) manufactured by Terra Systems, Inc.
  - Fast-release lactate creates reducing conditions soon after injection to kick-start the bioactivity
  - Emulsified oil dissolves slowly, releasing hydrogen to maintain reducing conditions, providing a longevity of three to five years
  - Emulsified oil is immobile after adsorbing to soil particles
  - SRS has the consistency of milk and comes ready for injection
  - Applied at the Seep Area to form long lasting BioBarrier and at SE Hot Spot 1, which has a high groundwater flow velocity

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Carbon Source – HRC-X

- Hydrogen Release Compound (extended release formula)
  - A proprietary polylactate ester manufactured by Regenesis Bioremediation Products, Inc.
  - A viscous material that slowly releases lactic acid
  - High viscosity at ambient temperature – needs to be heated for injection
  - Relatively immobile and does not migrate; ideal for aquifers with steep hydraulic gradients and/or high flow velocities
  - Extended release formula remains active for multiple years
  - Applied at SE Hot Spot 2, which has a high groundwater flow velocity
  - Provides a side-by-side comparison with SRS at SE Hot Spot 1

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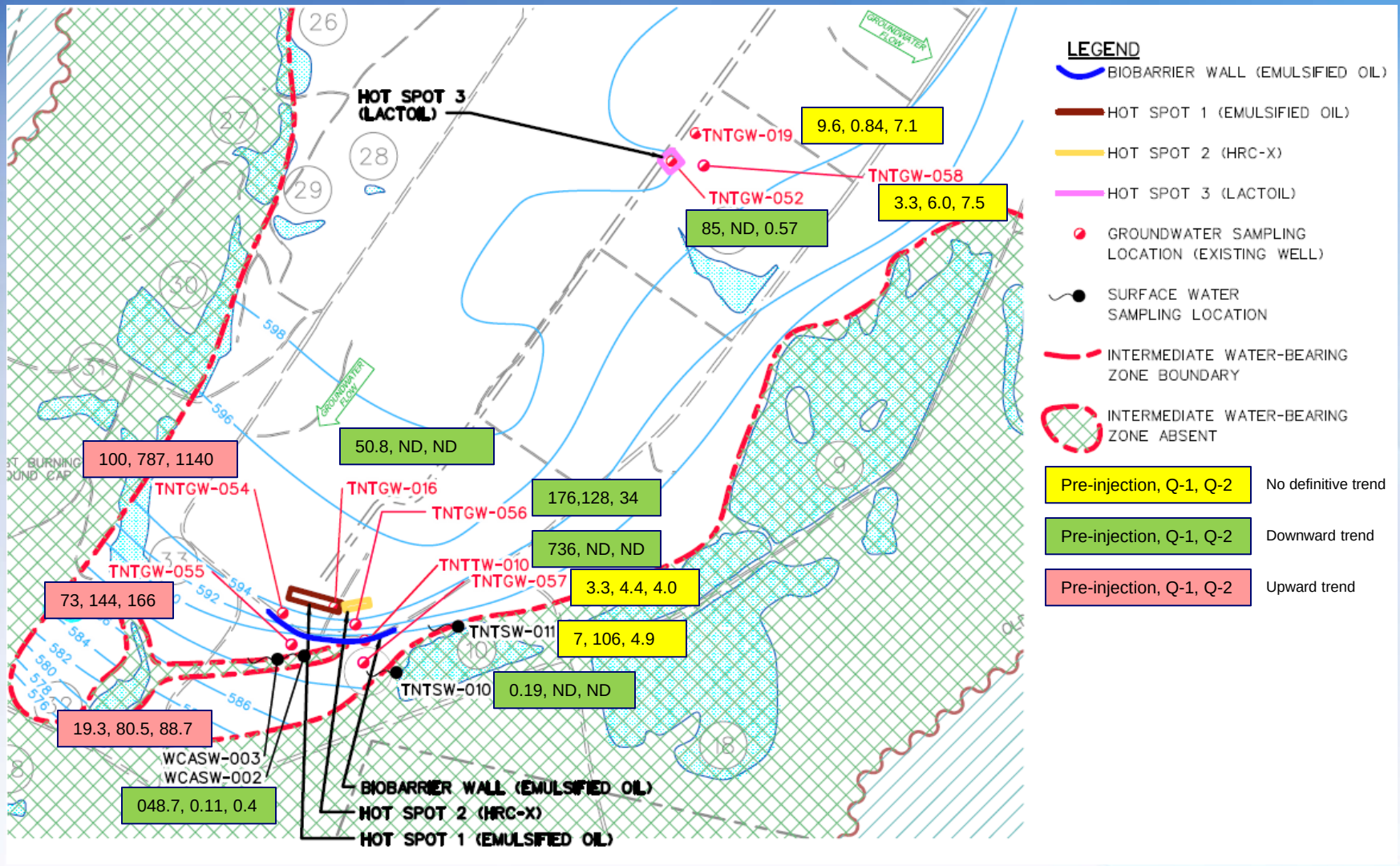
Carbon Source – LactOil

- A mixture of ethyl lactate (40%) and vegetable oil (40%) manufactured by JRW
- Ethyl lactate generates more metabolic acids per unit weight than sodium lactate. It has the potential to reduce pH, thus requiring pH buffering
- One micrometer oil droplet compared to 5-10 micrometers in common emulsified oil, moves through pore space more easily, but also has a shorter active life
- Applied at SE Hot Spot 3 where COC concentrations are lower and longevity is not as critical

TNT Concentration Trends to Date



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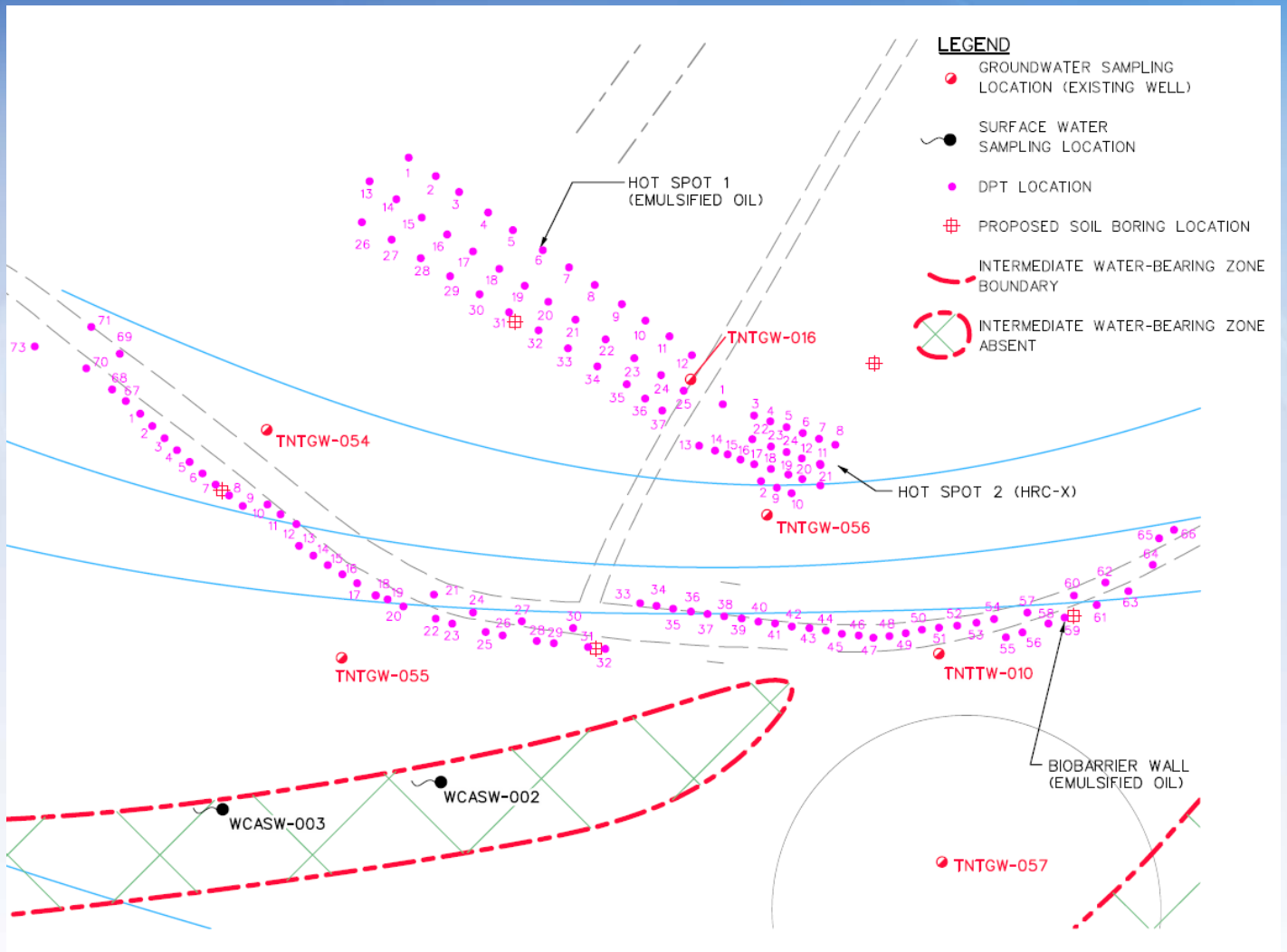
Seep Area – BioBarrier Installation

- SRS injected in a linear pattern perpendicular to groundwater flow
- Forms a long-lasting BioBarrier to intercept groundwater flow and prevent downgradient migration of COCs to the seeps
- BioBarrier consists of 72 injection points with a 10-foot spacing
- A total of 32,791 lbs of SRS was mixed with potable water to provide 20,000 gallons of solution for injection
- 197 lbs of yeast extract was added as a nutrient
- ~308 gallons of solution (35% of available pore volume) was injected at each point
- A target injection interval of 10-18 feet below ground surface was adjusted 10 feet deeper for a few points based on lithology
- Surfacing occurred at several injection points due to local lithologic variations

Seep Area – BioBarrier Installation

BioBarrier Layout



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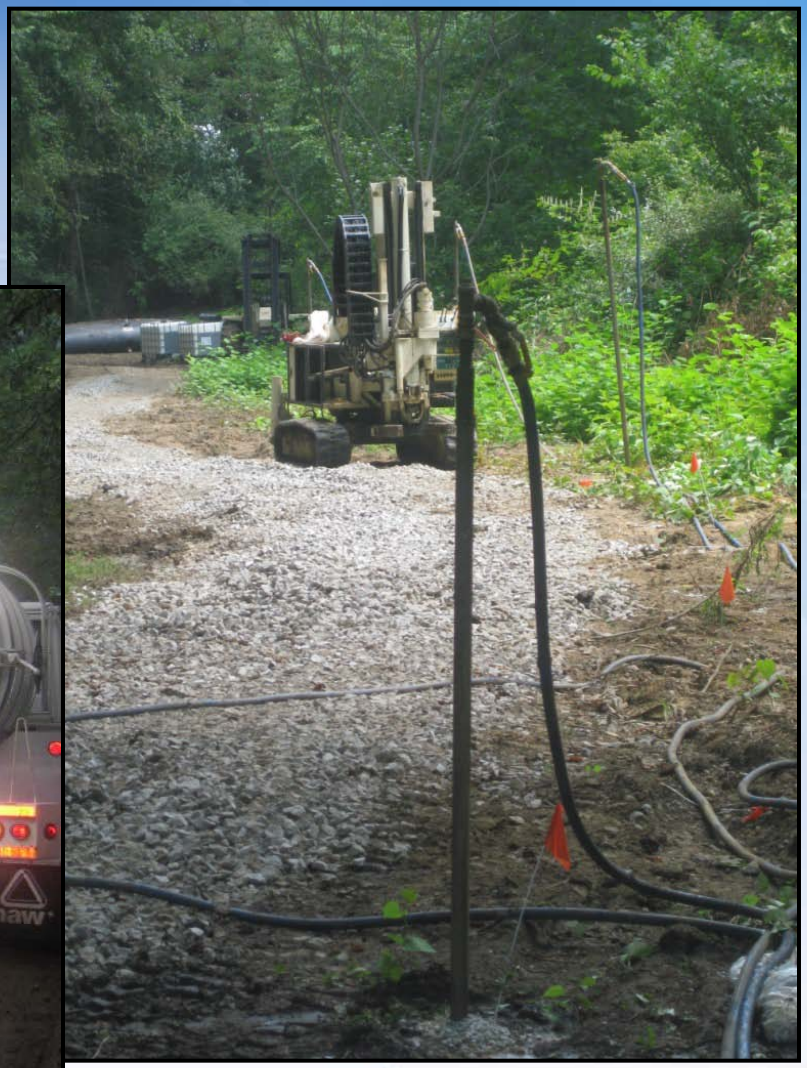
BioBarrier SRS Mixing and Injection



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BioBarrier Installation and Impact at the Seep Area

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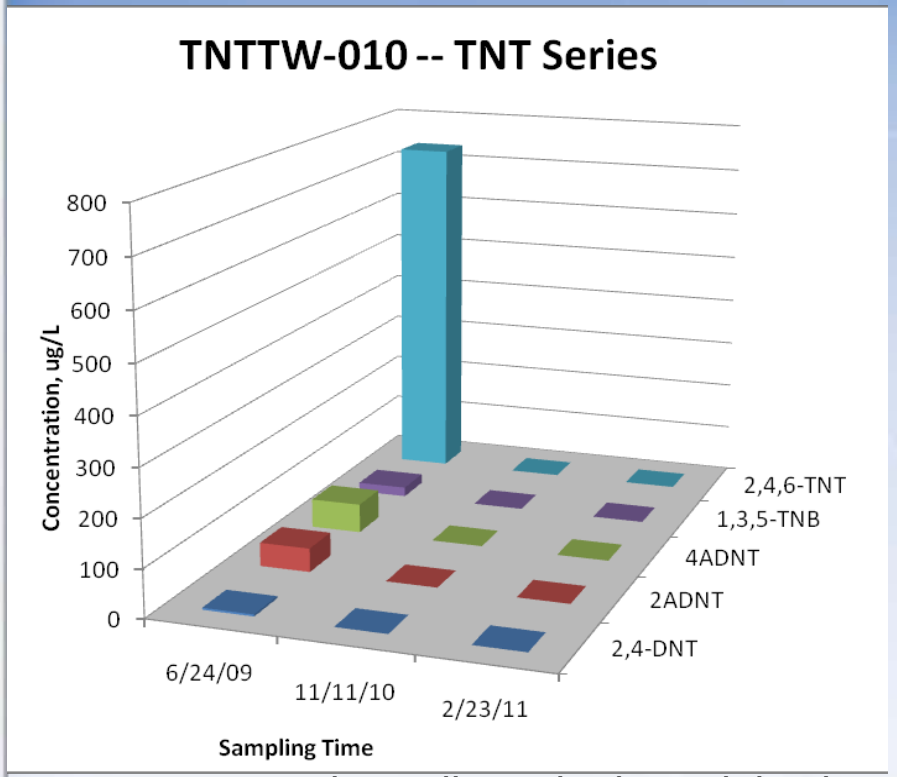
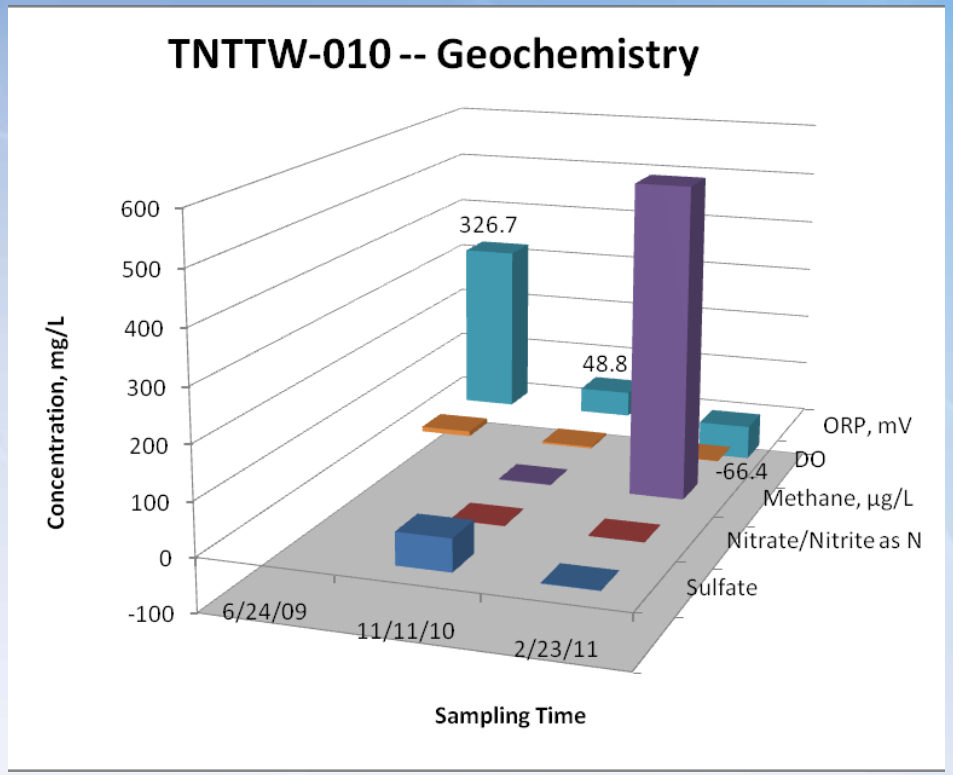
BioBarrier Results – Within the Injection Array





- Water samples collected prior to injection and every three months after injection
- TNT series compounds decreased to below detection limit of 20 ug/L three months after injection.
- ORP dropped from 326.7 to -66.4 mV, DO from 9.7 to 0.72 mg/L, sulfate from 59.9 to 1.2 mg/L, and methane increased from 1.4 to 580 mg/L.

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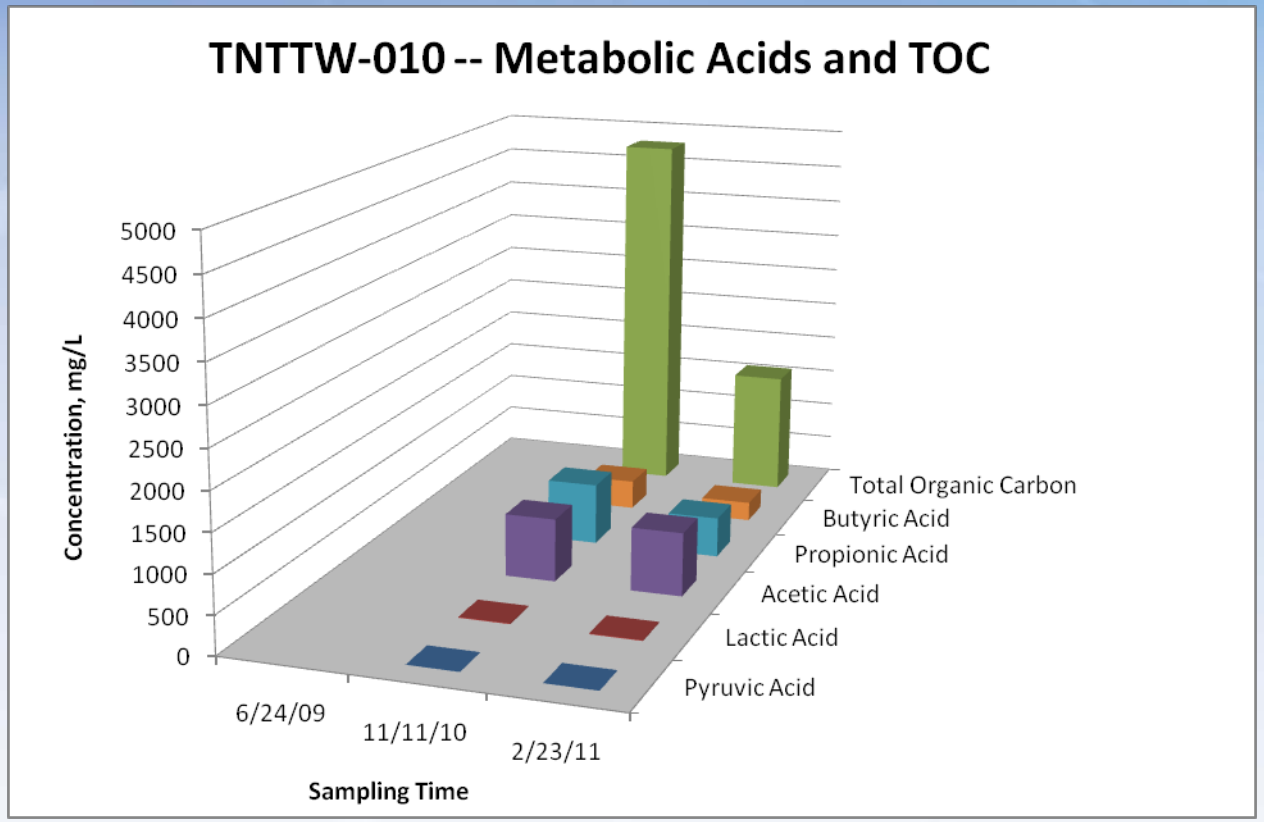
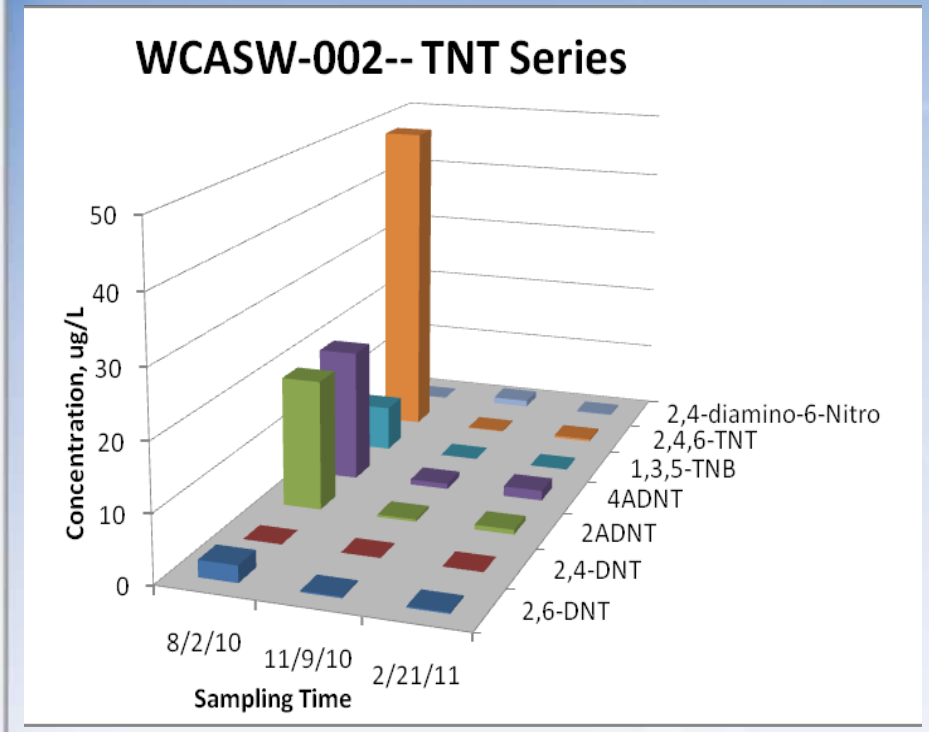
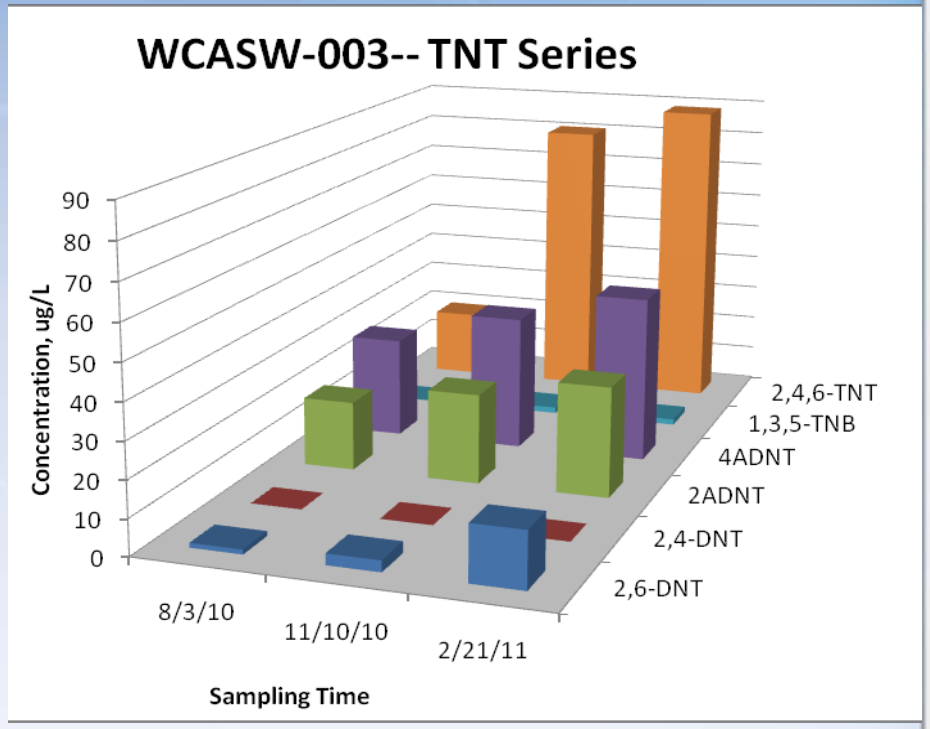
BioBarrier Results – Within the Injection Array



- TOC increased to 4,800 mg/L, and gradually decreased to 1,600 mg/L
- Metabolic acids increased to 820 mg/L, gradually decreasing

BioBarrier Results – Downgradient Seeps





- More than 90% reduction of TNT series immediately downgradient at the seep location (WCASW-002)
- Further downgradient at seep location WCASW-003, increasing trend of degradation intermediates including 2ADNT, 4ADNT.

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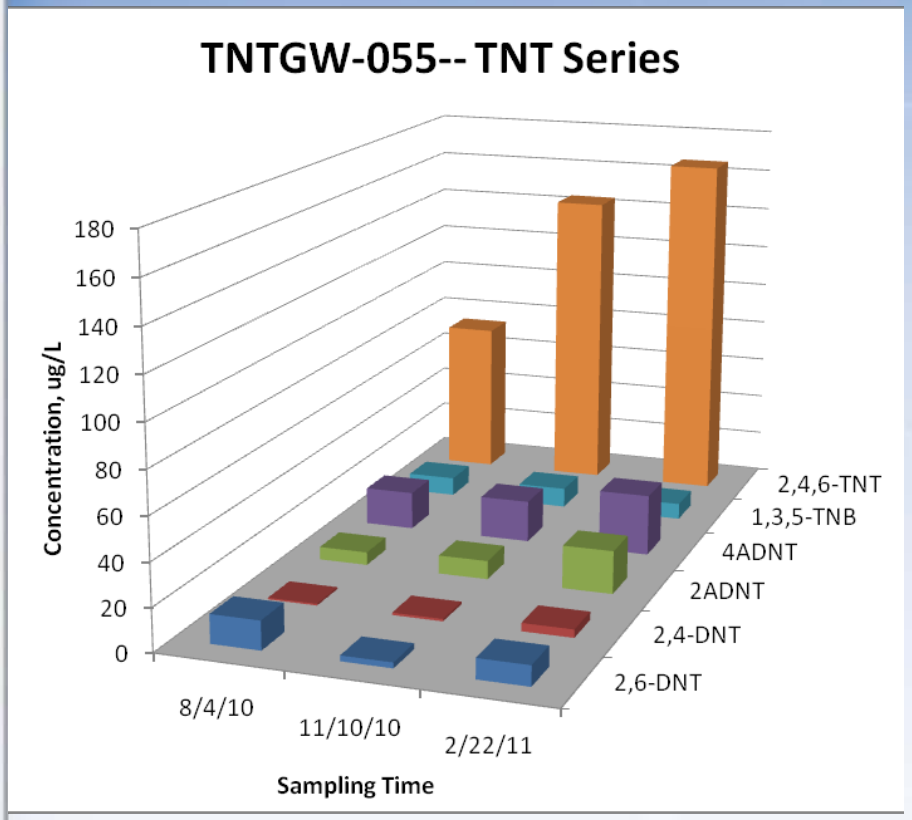
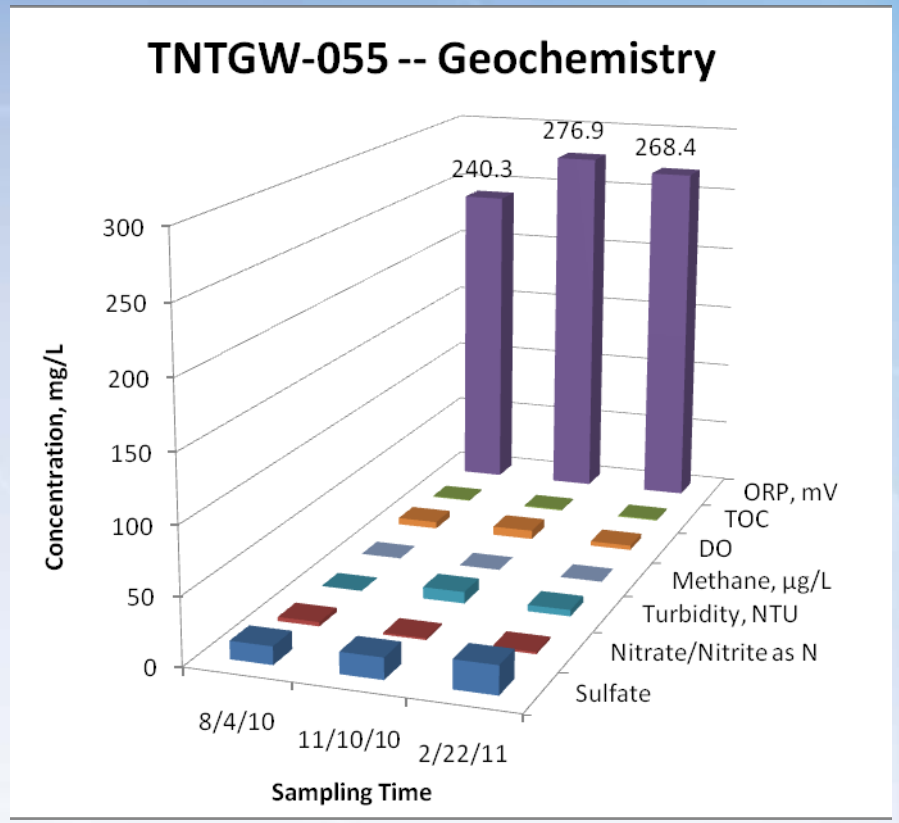
BioBarrier Result – Downgradient TNTGW-055





- Increasing concentrations of nitroaromatics observed at TNTGW-055

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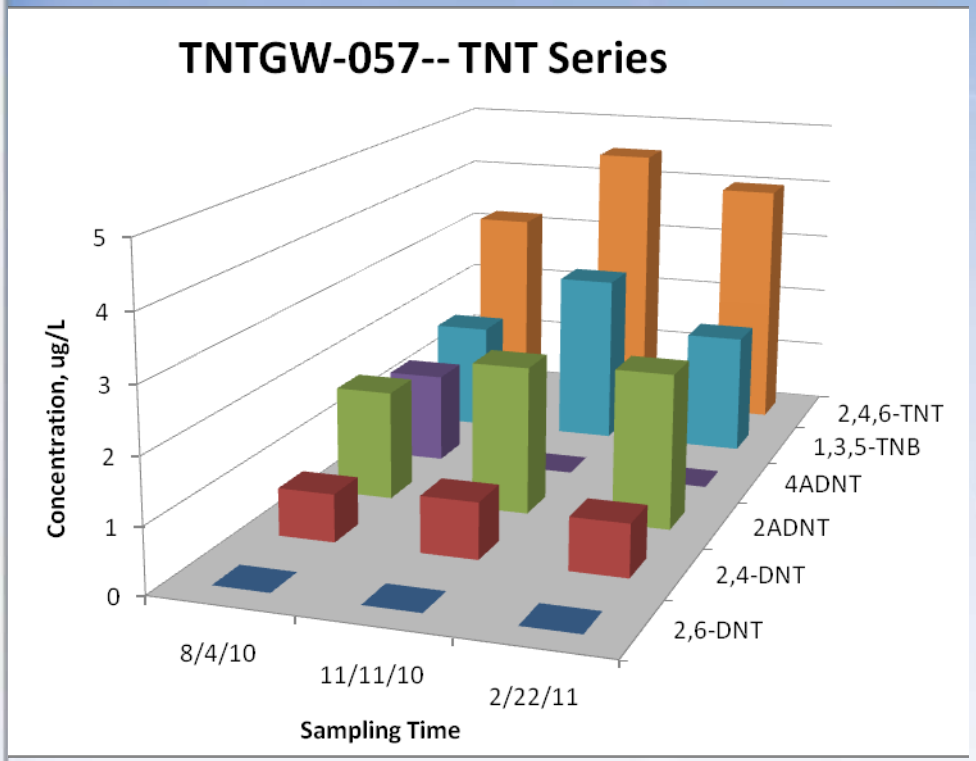
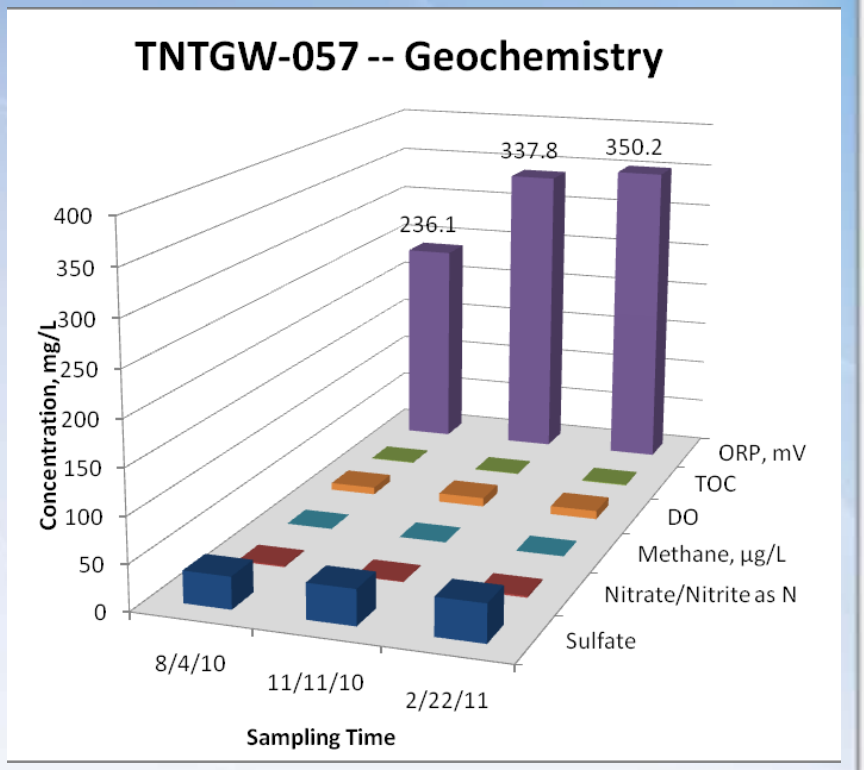
BioBarrier Result – Downgradient TNTGW-057





- No significant impact observed in the first two quarterly sampling events at TNTGW-057

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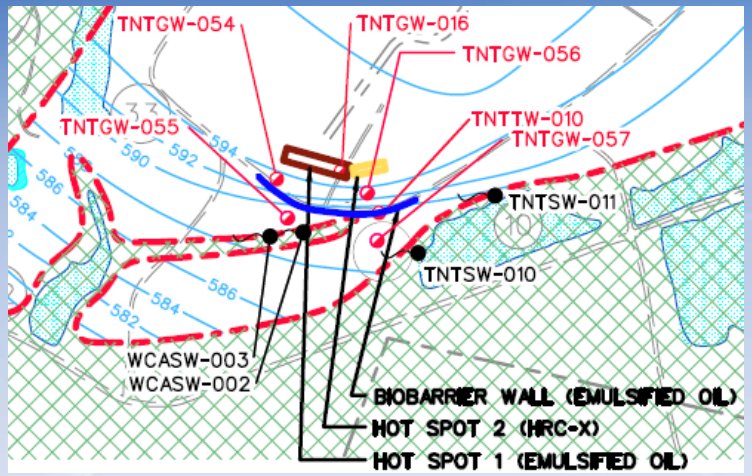
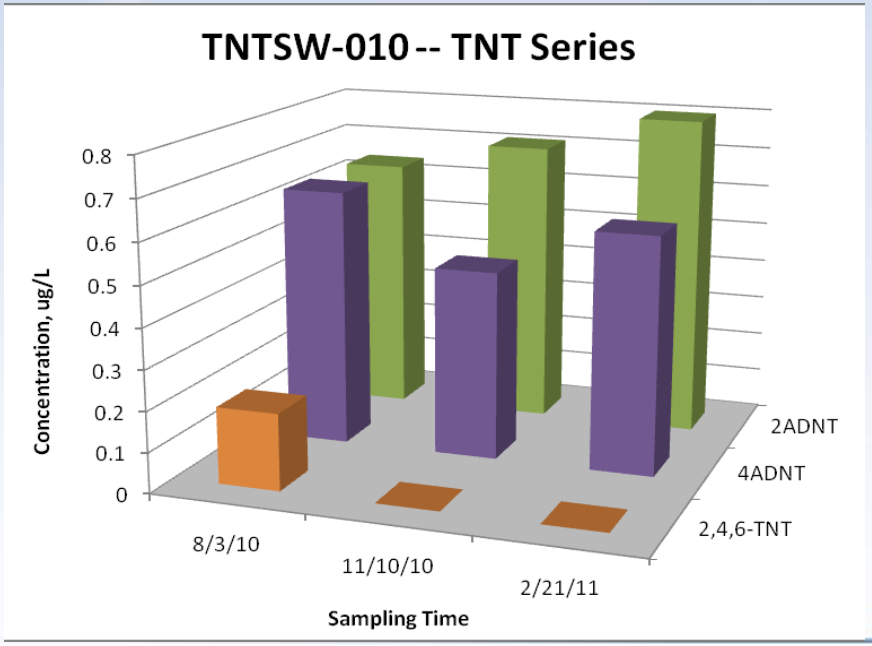
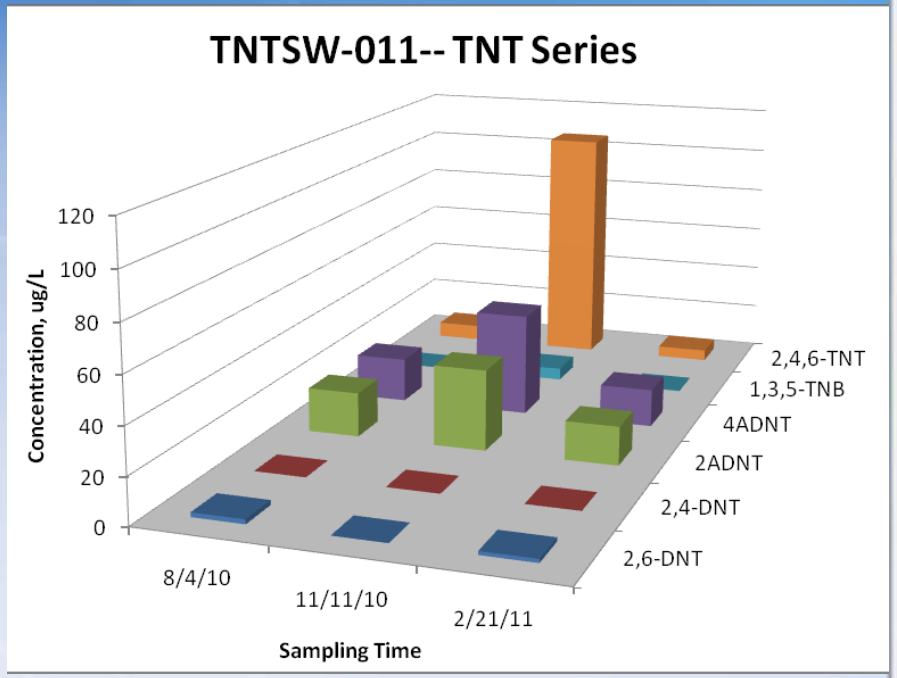
Other Surface Water Samples







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SE Hot Spot 1 Area

- Located upgradient of the western portion of the BioBarrier
- High TNT concentration (156 ug/L), and relatively high groundwater flow rate (0.5 feet/day) → suitable for SRS
- A total of 17,867 lbs of SRS was mixed with potable water to provide 11,400 gallons of solution for injection at 37 points
- 107 lbs of yeast extract was added as a nutrient
- ~308 gallons of solution was injected at each point

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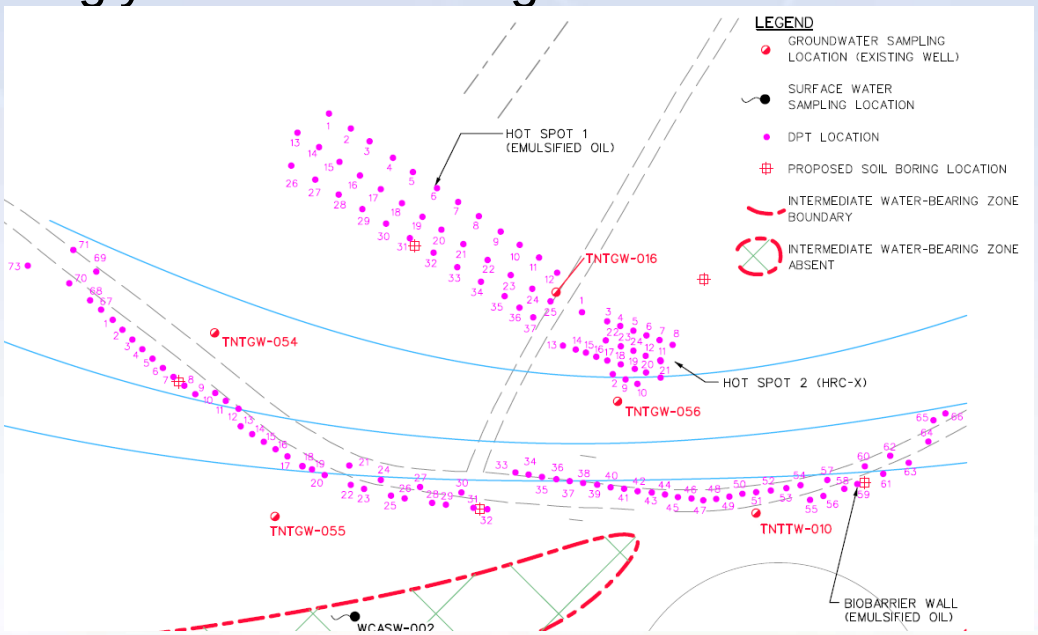
SE Hot Spot 1 SRS Injection

- 250-foot × 50-foot injection grid
- ~200 feet upgradient of the western portion of the BioBarrier (~ one year of groundwater travel time)
- Total of 37 injection points aligned in three parallel rows
- Target depth interval of 10-18 feet below ground surface, adjusted accordingly based on changes in elevation



SE Hot Spot 1 Injection

SE Hot Spot 1 Injection

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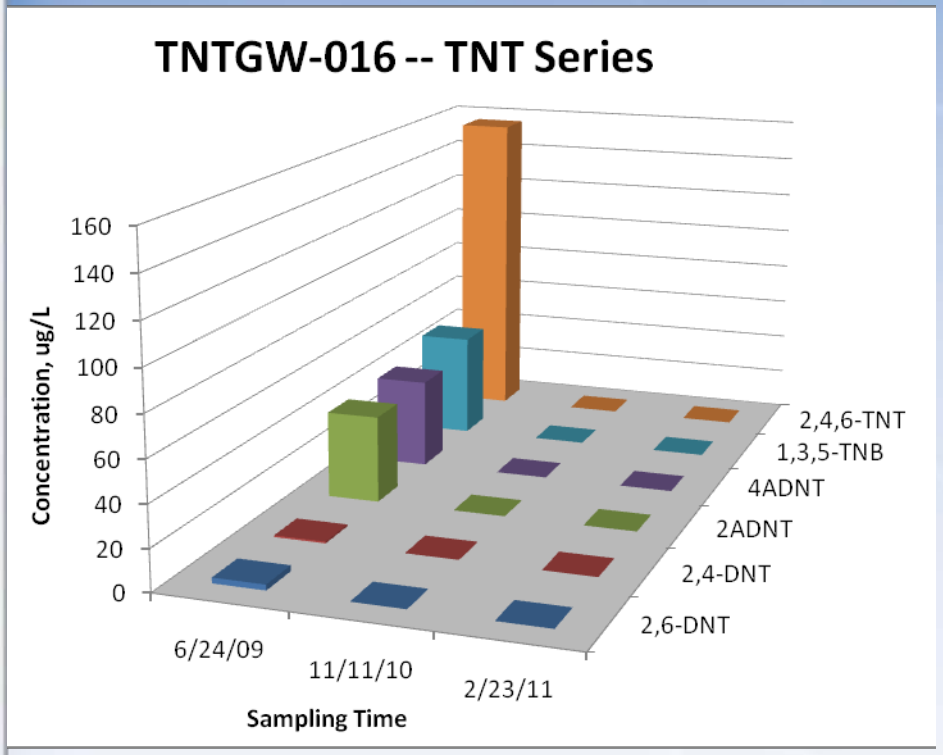
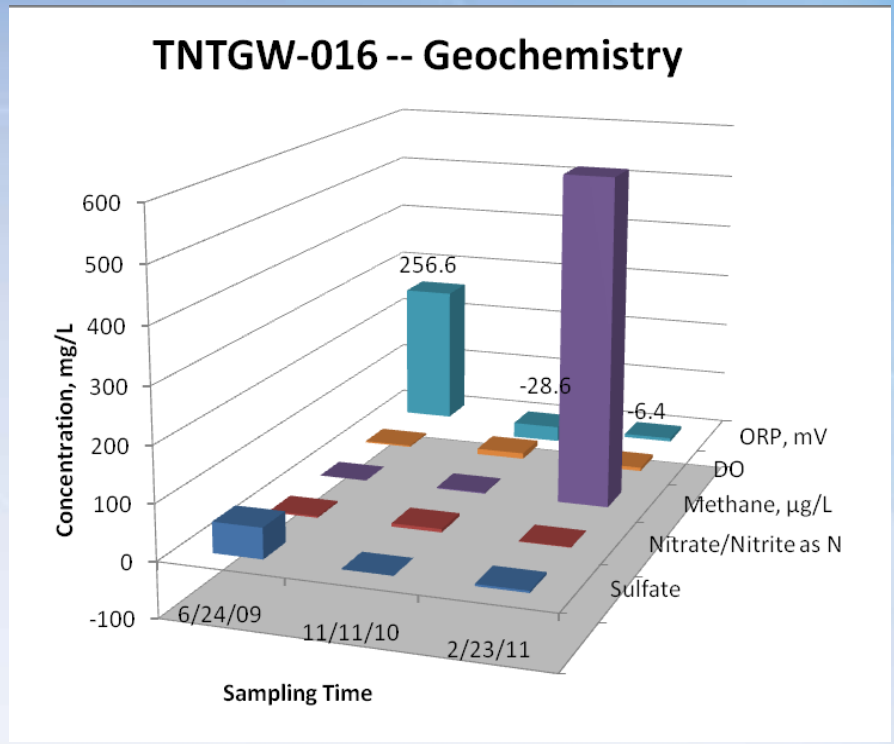
SE Hot Spot 1 Results – Within the Injection Array





- Water samples collected prior to injection and every three months after injection
- TNT series compounds decreased to below detection limit of 20 ug/L
- ORP and sulfate decreased; methane generated (592 mg/L)

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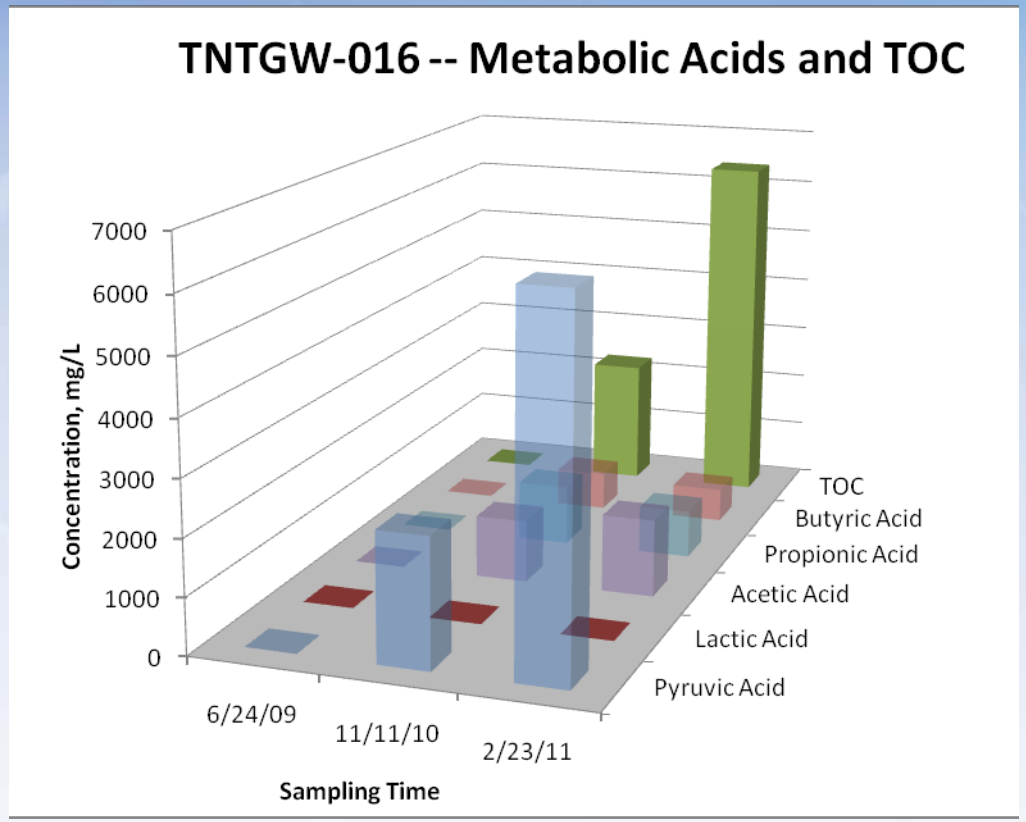
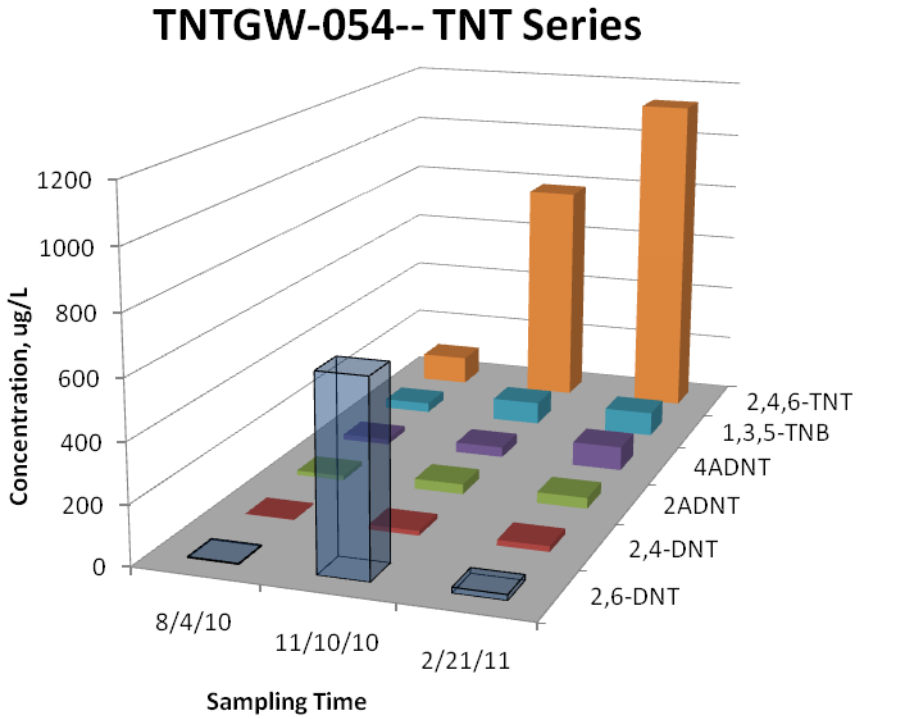
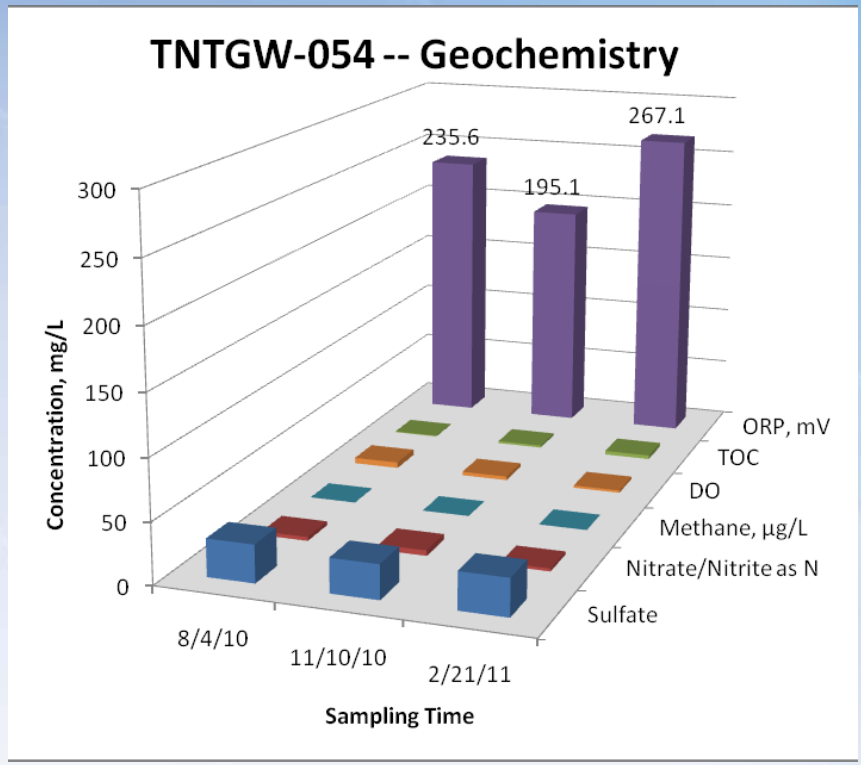
SE Hot Spot 1 Results – Within the Injection Array



- TOC have increased from 1.1 mg/L to 6,400 mg/L
- Metabolic acids have increased to 1,380 mg/L

SE Hot Spot 1 Results – Downgradient Monitoring Well





- Increase of some TNT series compounds – a slug of contaminated groundwater was likely pushed toward this monitoring well during BioBarrier injection

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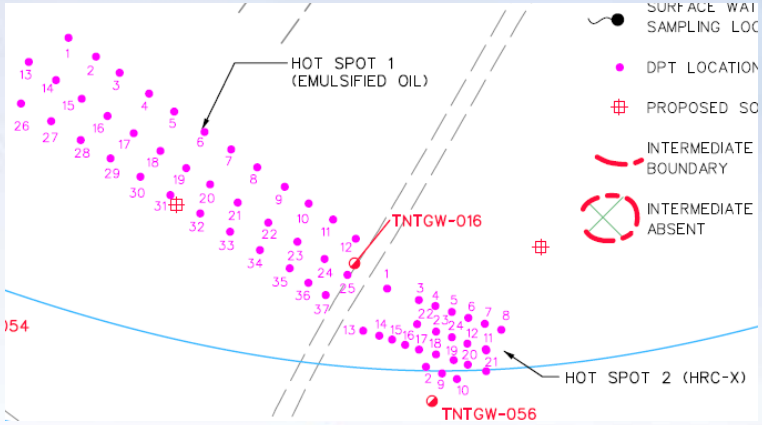
SE Hot Spot 2 Area

- Located upgradient of the central portion of the BioBarrier
- High TNT concentration (156 ug/L) and relatively fast groundwater flow (0.5 feet/day)
- HRC-X selected for this area → side-by-side comparison with SRS (SE Hot Spot 1)
- A total of 810 lbs of HRC-X was injected through 24 points (~34 lbs for each point)
- HRC-X was heated to 160°F in a hot water bath to reduce viscosity prior to injection; no dilution required

SE Hot Spot 2 HRC-X Injection

- A 100-foot × 50-foot injection grid
- ~180 feet upgradient of the BioBarrier (~ one year of groundwater travel time from SE Hot Spot 2 to BioBarrier)
- Total of 24 injection points spaced on 10-foot centers, aligned in four rows based on accessibility, in a staggered configuration
- Target depth interval of 3-8 feet below ground surface at the lowest elevation points, adjusted accordingly at higher elevations



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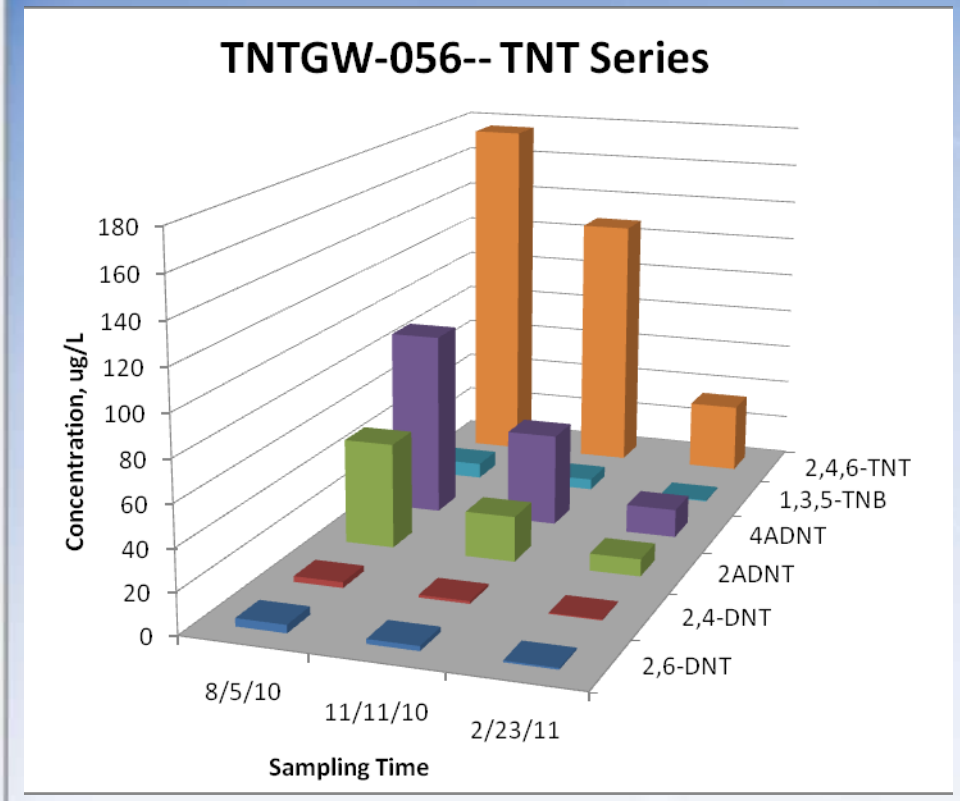
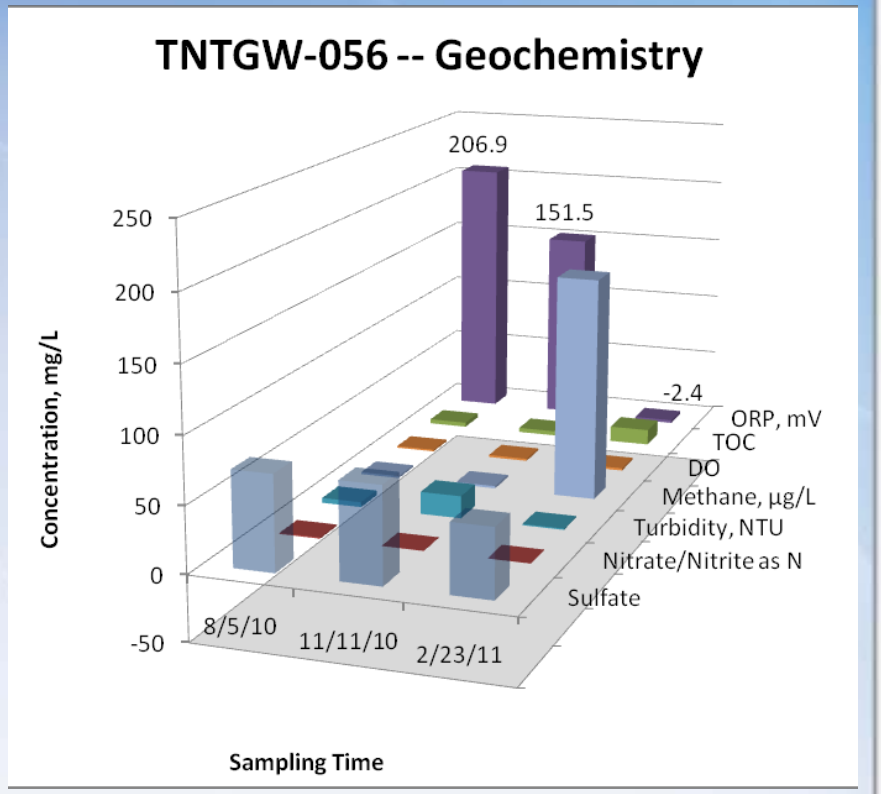
Heating HRC-X

SE Hot Spot 2 Injection

SE Hot Spot 2 Results – Downgradient Monitoring Well





- Decrease in TNT from 176 to 34.3 ug/L
- Steady decrease in ORP from 206.9 mV to -2.4 mV
- Slight decrease in sulfate in second quarterly post-injection sample

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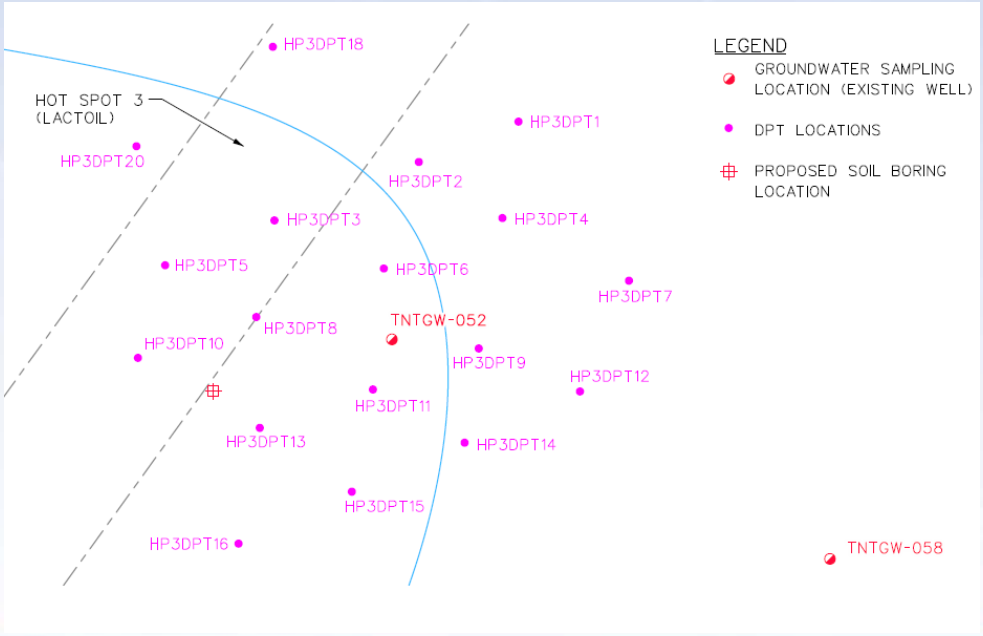
SE Hot Spot 3 Area - LactOil Injection

- Soil treatment (blending/removal) was conducted previously in this area
- Groundwater flow velocity 0.58 feet/day at nearby well TNTGW-019
- Relatively low TNT concentration (85 ug/L) – no critical requirement on carbon source longevity
- LactOil with relatively short life-span was selected as the carbon source
- A total of 5,714 lbs of LactOil was mixed with potable water to produce 3,500 gallons of solution for injection through 18 points (~200 gallons at each point)
- 34 lbs of yeast extract was added as a nutrient
- 300 lbs of $NaHCO_3$ added as a pH buffer

SE Hot Spot 3 LactOil Injection

- A 80-foot × 80-foot injection grid
- Sixteen injection points in four staggered rows
- Due to surfacing at some points, two points were added in the field to achieve the design injection volume
- Target depth interval of 10-15 feet below ground surface at the lowest elevation points was adjusted accordingly at the higher elevation points



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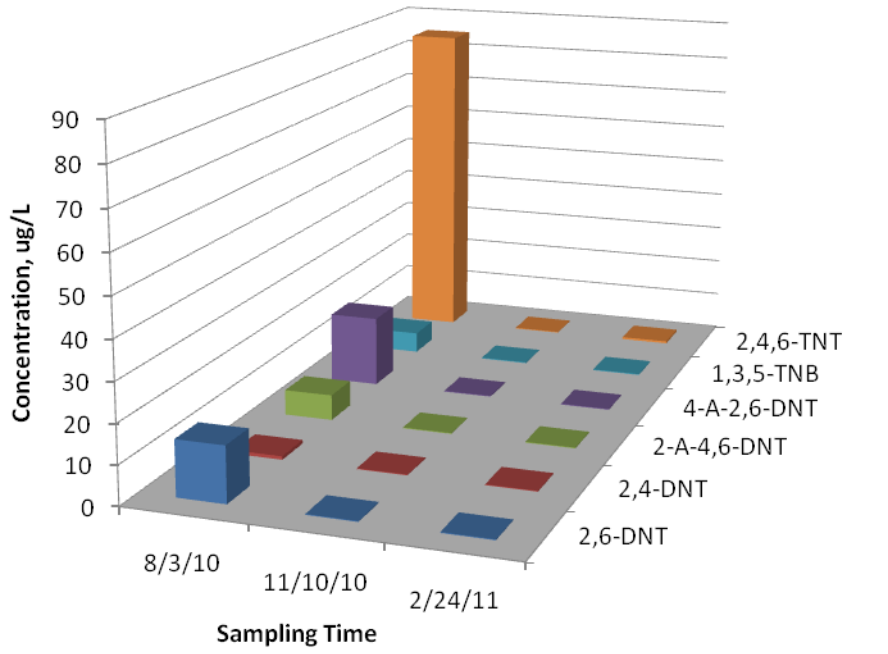
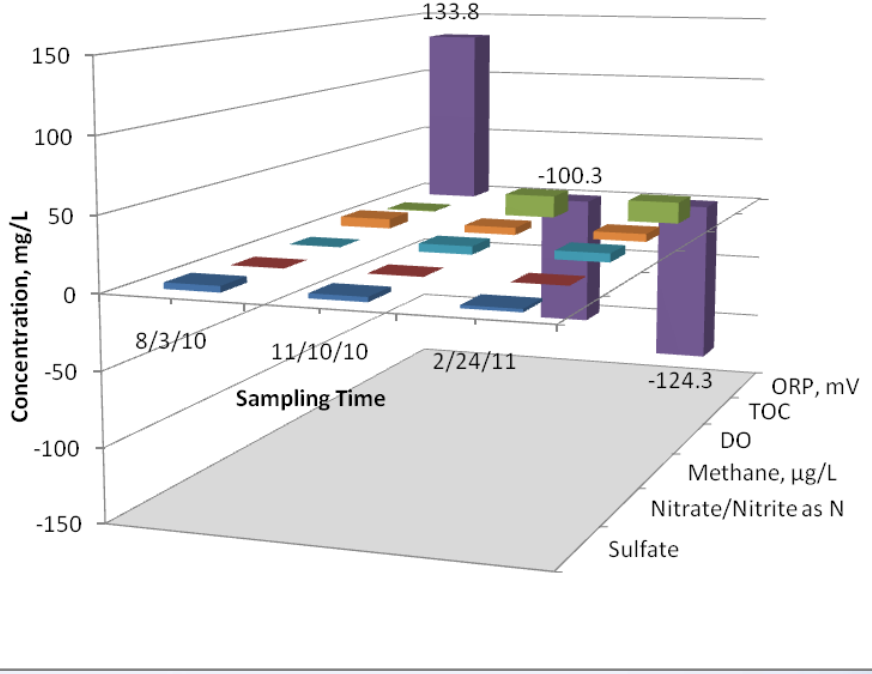
SE Hot Spot 3 Injection

SE Hot Spot 3 Results – Within the Injection Array





- TNT series compounds decreased to below detection limit of 0.20 ug/L
- ORP and DO decreased; TOC and methane increased
- No metabolic acids detected to date

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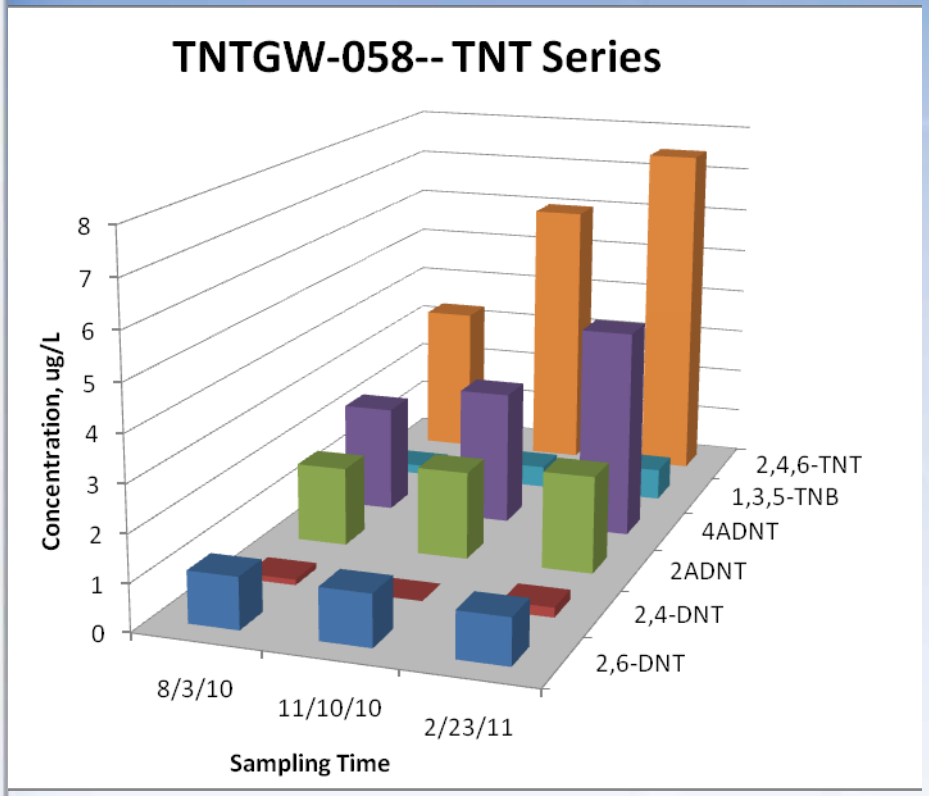
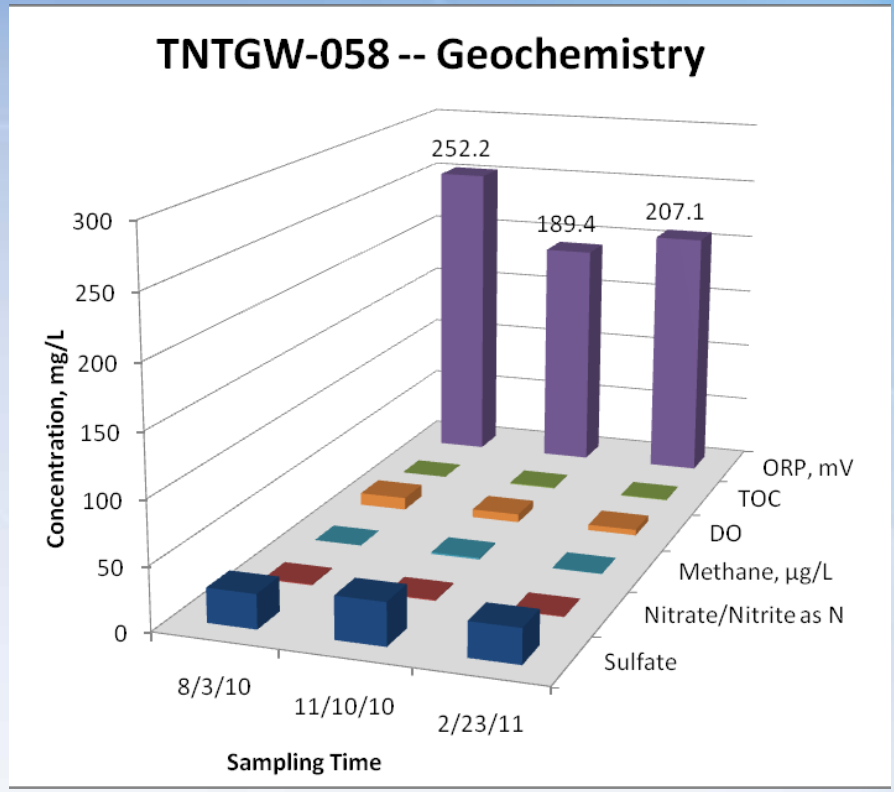
SE Hot Spot 3 Results – Downgradient Monitoring Well





- No downgradient impact six months after injection

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Comparing Performance of SRS, HRC-X and LactOil

Parameters	SRS		HRC-X	LactOil
	TNTTW-010 Biobarrier	TNTGW-016 SE Hot Spot 1	TNTGW-056 SE Hot Spot 2	TNTGW-052 SE Hot Spot 3
Sulfate, mg/L	1.2	3.8	51.9	2.1
Nitrate/Nitrite as N, mg/L	<0.05	0.9	0.11	< 0.05
Methane, µg/L	580	592	171	6240
ORP, mV	-66.4	-6.4	-2.4	-124.3
DO, mg/L	0.72	6.45	1.85	5.77
TOC, mg/L	1,600	6400	12.3	16.3
Pyruvic Acid, mg/L	1	< 1	< 0.1	< 0.1
Lactic Acid, mg/L	10	< 10	< 1	< 1
Acetic Acid, mg/L	824	1,380	< 1	< 1
Propionic Acid, mg/L	519	853	< 1	< 1
Butyric Acid, mg/L	247	607	< 1	< 1

- Both SRS and LactOil decreased TNT series compounds to below detection limits within the injection grids
- Down-gradient of HRC-X injection grids showed a steady decrease of TNT series in the first two quarterly samples
- All three substrates successfully created reductive conditions at the designed dosing rates
- LactOil generated a spike of methane and lowest ORP– short bloom of electron donors
- SRS generated two orders of magnitude higher TOC and metabolic acids – long-lasting slow release carbon source

Conclusions

- EISB is shown to be effective for treatment of ground water contaminated with nitroaromatics
- Carbon source selection was based on several factors
  - Hydraulic gradient and ground water flow velocity
  - Contaminant concentrations
- The designed dosing rates of carbon sources were able to create reducing conditions within the injection zones
  - Negative ORP values
  - Decreasing DO and sulfate
  - Increasing methane and metabolic acids
  - Contaminants decreased to below detection limits
- No downward trend in concentration observed downgradient of SRS injection area in the first two quarterly sample rounds
- Downward trend in concentration observed at the seep location nearest the BioBarrier, and down gradient of the HRC-X treatment area
- Pilot-scale field application provides valuable information for carbon source selection and full-scale design parameters

Questions?